Synthesis of silver bromide ultra fine-crystalline suspensions

Agnieszka DYONIZY, Piotr NOWAK, Agnieszka KRÓL-GRACZ, Ewa MICHALAK – Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wrocław

Introduction

Researches into the synthesis and physicochemical properties of silver halide crystals have been undertaken for many years. In traditional photosensitive materials such crystals are used as highly effective light sensors, and despite the rapid development of digital image recording, they have remained irreplaceable in some applications such as autoradiography, industrial flaw detection techniques or medical diagnostic procedures [1-3]). Traditional photosensitive materials contain halide crystals of size ranging from 0.1 to 10 μm, while crystals in the size range between 10 and 100 nm have so far been used only in special application materials, such as holography, microelectronics and technological photography. Photosensitive materials containing nano-size particles are known in both science and literature as Lippmann emulsions. They are characterised by high contrast, high resolution and image sharpness, while retaining low general photosensitivity, which in turn results in low granularity.

Recently observed increasing interest in this type of crystals is a result of unique properties, including optical, electrical, mechanical and others, silver halide nanocrystals possess [4-8]). Furthermore, silver halide nanocrystals are a useful substrate in synthesising of nanostructural silver, either by using mild reduction or spectrally sensibilised crystal photolysis, resulting in metallic silver characterised by colloidal or nanocolloidal dispersion. Therefore, particle size distribution properties of ultra fine-crystalline silver bromide suspensions play a pivotal role in the suitability of such suspensions as substrates for producing nanostructural silver, especially when obtained as highly concentrated, preferably monodispersive sols, containing a non-toxic continuous phase. Further descriptions of synthesis, properties and applications of nanostructural silver can be found in numerous scientific and technological publications [9-11]).

The main objective of the planned research has been determining conditions required for preparation of highly concentrated suspensions of silver bromide crystals, characterised by containing crystals of size no larger than 100 nm. Research was conducted using a method for producing ultra fine crystalline suspensions of silver halides as described in [12-15], appropriately modified and optimised for obtaining silver bromide crystals as small as possible [16].

Experimental part

Crystalline silver bromide suspensions were prepared in water solutions of photographic gelatine – a natural protective colloid, strongly impeding silver halide crystals formation. The degree of crystals formation retardance, described by PR value (*Physical Retardance*), can be determined using *PAGI METHOD* standards [17]. When applied to Lippmann suspensions, PR value should not exceed 60. To produce the smallest possible, thermodynamically stable crystal seeds, synthesis was conducted at optimal low temperature [18], set at 35°C. The reaction vessel was equipped with a potentiometric measurement system, allowing for measuring and recording of bromide ions activity changes during the process. A spectophotometric immersed probe, with a light pathway of 2 mm, was installed besides the potentiometric electrodes, which allowed for direct measurements of spectral influence on solution turbidity during the course of the synthesis. Such measurements allow the analysis of various phenomena during the syn-

thesis, i.e. crystal seeding, Ostwald recrystallisation and silver bromide crystals growth. Measurements concerning the influence of substrate dosing speed into the dispersive solution on size of silver bromide crystals were undertaken in the same set of experimental conditions. Dosing speed was regulated by modification of molar concentrations of silver nitrate ($AgNO_3$) and potassium bromide (KBr) in the solutions. Reactant concentrations were varied in range of 0.4 to 3.5 mol/dm³.

Precipitation of suspensions was conducted using a mechanism described by Figure 1, which shows a schematic system of alternate reactant introduction into the dispersive solution. 100 cm³ of intensely stirred 5% (weight) gelatine solution (sol. 1, Fig. 1), present in the reaction vessel, was introduced alternately at 20 minutes intervals with 10 cm³ of silver nitrate solution (sol. 2, Fig. 1) and potassium bromide (sol. 3, Fig. 1). The process of precipitation was carried out throughout 15 cycles; a single cycle being the introduction of a single dose of silver nitrate solution and potassium bromide solution each. After finishing each full cycle of dosing, before beginning the next, the crystalline system was set aside for approximately 5 s to allow homogenisation and stabilisation of physicochemical conditions throughout the whole reaction vessel. The overall timespan of a properly carried out precipitation did not, in general, exceed 11.25 min. Towards the end of precipitation, excess bromide ion concentration was stabilised, setting their activity at pBr=3.5, the suspension was further stabilised by addition of gelatine in an amount ensuring its final concentration as 5 g per 100 cm³ of suspension. Afterwards the suspension was divided into two equal parts and cooled to form a permanent gel structure. One part was stored at 2°C, while the second was ground mechanically and washed out with cold, clean water to remove excess salts present in the gel. The extent of purification was controlled by using a salinity meter. Washing was stopped after obtaining salinity lower than 20 ppm. The next step was washing the gel a number of times using distilled water containing potassium bromide at 3.16·10⁻⁴ mol/dm³ (pBr=3.5). After salinity has been stabilised with bromide ions, excess water was removed and the gel was molten and homogenised at 50°C. After being cooled down again, it was stored at the same temperature as the non-purified gel. After a number of days in storage, both gels' turbidities were analysed to assess the influence of Ostwald recrystallisation on silver bromide crystals size growth, in conditions associated with high post-reactive salinity (unpurified part) and in conditions of optimally lowest silver bromide solubility in water (purified part).
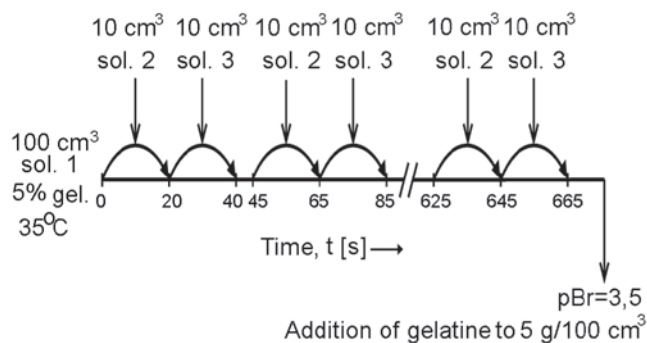

Fig 1. Scheme of preparing of ultra-fine silver bromide crystals suspension, so-called the Lippmann's emulsion
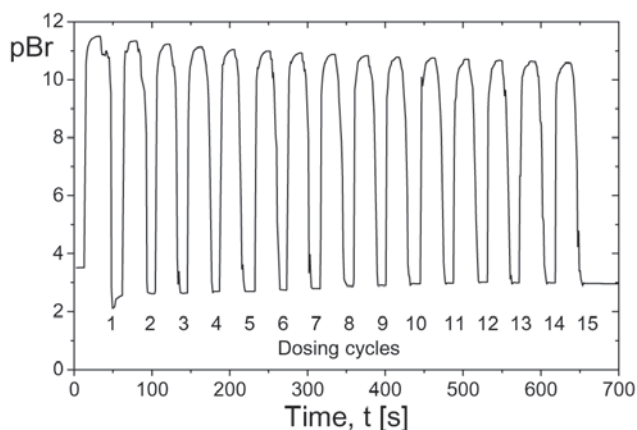
Fig. 2. An example of changing bromide ions activity, recorded during precipitation of a suspension of silver bromide crystals, from solutions of reactants of 1.0 mol/dm³ concentration. The process of precipitation was carried out throughout 15 cycles
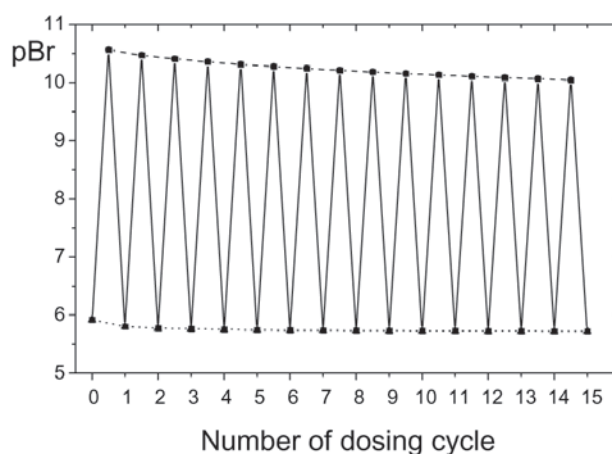

Fig. 3. Theoretically calculated fluctuations in bromide ions activity during synthesis of silver bromide crystals suspension, from solutions of reactants of 1.0 mol/dm³ concentration. The process of synthesis was carried out throughout 15 cycles

Figure 2 illustrates an example of changing bromide ions activity, recorded during precipitation of a suspension of silver bromide crystals, from solutions of reactants of 1.0 mol/dm³ concentration. Almost even fluctuations in extremes of the activity function, corresponding to concentration of excess bromide ions, let us conclude, that each consequent reagent dosing cycle resulted in seeding of a new crystalline phase, in conditions of very similar supersaturation and concentration of excess bromide. The clearly apparent drop in bromide ion activity maximum and the small, albeit visible increase in activity at the fluctuation minimum results from systematic increase in ionic strength of the crystallising mixture during the course of the whole crystallisation process.

Increasing ionic strength results in lowering of the activity of ions present in the mixture, which -due to the solubility constant- results in increasing silver bromide solubility (salt effect). Such phenomena induce seeding and recrystallisation of a new phase, forming during consequent dosing, which in turn manifests as, among others, a small, albeit consistent crystal growth. Figure 3 shows theoretically calculated fluctuations in bromide ions activity during synthesis of silver bromide crystals suspension, in theoretical conditions identical to those, for which real activity changes were registered (Fig. 2).

Ensuring consistent conditions for seeding and recrystallisation of the newly emerged phase in subsequent dosing cycles, is essential in producing highly homogeneous silver halide crystals suspensions, and, even more so, for fine crystals suspensions. Evaluation of bromide ions activity in several experimental suspension syntheses, using reactant solutions of various concentrations, and comparing experimental data with theoretical calculation results, confirmed that both the theoretical assumptions pertaining to the synthesis scheme, as well as the reaction method were correct. It can be therefore concluded, that synthetic methods used in this work for synthesising ultra fine-crystalline suspensions of silver bromide, namely cyclic, precise dosing of reactant solutions into the dispersive solution of known volume and gelatine concentration, fulfil the required criteria and may be used to conduct research as planned.

Laboratory experiments were based on preparing a set of eight Lippmann suspensions and evaluating the influence of crystallising mass introduction speed into the reacting mixture, on the average size of crystals formed in the final stages of suspension synthesis (after the 15th cycle). Synthesising such suspensions required the use of water solutions of silver nitrate ($AgNO_3$) and potassium bromide (KBr) in the following concentrations: 0.4; 0.5; 1.0; 1.5; 2.0; 2.5; 3.0 and 3.5 mol/dm³. Additionally in each experiment, changes in current silver bromide crystals size were recorded, in each subsequent dosing cycle, using turbidity measurements of the crystallising solution registered during the synthetic process. Further work presents results of analyses

carried out on a suspension prepared using solutions of concentrations equal to 1.0 mol/dm³.

The size of silver bromide crystals were determined by turbidity measurements using two methods. The first method involved measuring real-time spectral changes in turbidity of the crystallising medium, for wavelengths: 500, 600, 700 and 800 nm and evaluating values of specific turbidity after each dosing cycle. The average diameter of colloidal particles was then calculated using Rayleigh equation. The second method of measurements was based on the concentration method, using samples of the suspension taken after 5, 10 and 15 cycles of reactant dosing. To ascertain silver bromide crystals size, spectral turbidity dependence on concentration was prepared for each sample, and the results obtained were used to calculate specific turbidity, which in turn allowed for the calculations of average crystals diameter. Average particle diameter obtained in this manner was then used to calculate length of a cube edge (d_6) (during synthesis of Lippmann suspensions cubic crystals of silver bromide are formed). To remove the influence of self-absorption on measurements of silver bromide crystals size by turbidity measurements, calculations were made using data recorded at wavelength of 600 nm, therefore far from the silver bromide self-absorption wavelength of 490 nm.

Using the first method, the curves of changes in turbidity, registered while obtaining suspensions, were plotted, in wavelength range of 500 to 800 nm. An example of such dependence, determined for a synthesis using reagents 1.0 mol/dm³ concentrations, is shown on Figure 4. As it was previously mentioned, a single dosing cycle refers to introducing 10 cm³ of silver nitrate ($AgNO_3$) solution, and 10 cm³ potassium bromide (KBr) solution. In the initial stages of synthesis thermodynamically unstable crystal seeds form, which under the influence on rapid, alternating changes in reagent concentrations, dissolve and reform alternately. During subsequent dosing cycles, supersaturation of the solution reaches an advantageous value, which favours stable crystal seeds formation. Such crystal seeds grow to a size determined by the current value of supersaturation and bromide ion concentration. In the example (Fig. 4), new phase seeding and Ostwald recrystallisation can be observed after the third reagent dosing cycle.

A consistent increase in turbidity of crystallisation mixture, systematically in each dosing cycle, starting at cycle 4 and up to the end of synthesis at cycle 15, proves the thesis right. Figure 5 shows fluctuations in turbidity of the crystallisation mixture, evaluated for a wavelength equal to 600 nm.

Fluctuation maxima of the turbidity function correspond to the exact moment of introducing a portion of silver nitrate ($AgNO_3$) solution, while the function minima correspond to introduction of potassium bromide (KBr) solution. By introduction of KBr into the crystallising mixture, free bromide ions concentration increases, which in turn
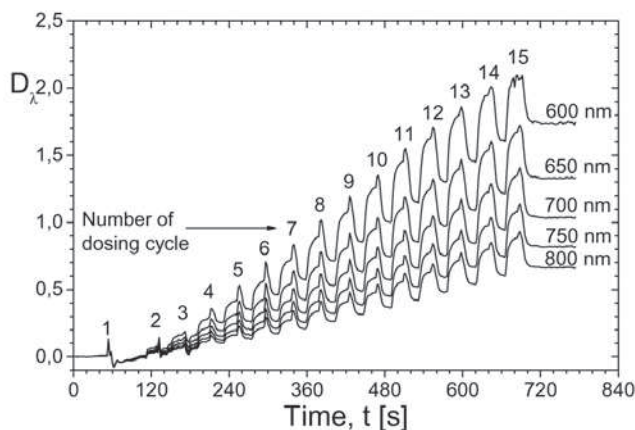
Fig. 4. Fluctuation in turbidity as optical density during synthesis of silver bromide crystals suspension, from solutions of reactants of 1.0 mol/dm³ concentration. Dependence was calculated at wavelengths: 600, 650, 700, 750 and 800 nm.
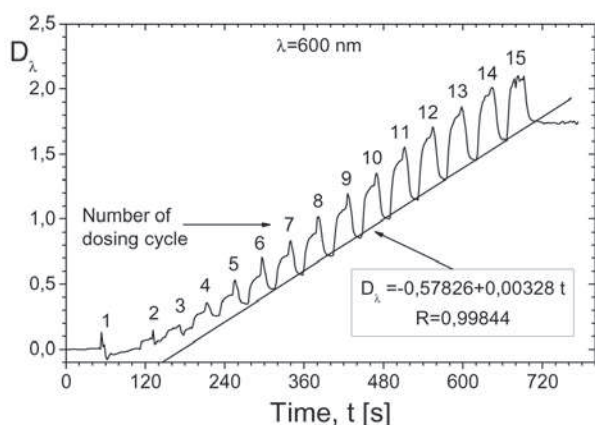

Fig. 5. Fluctuation in turbidity measured at 600 nm during synthesis of silver bromide crystals suspension, from solutions of reactants of 1.0 mol/dm³ concentration. Straight line was fitted to values of optical density, which corresponded to 5 seconds periods of stabilization of crystallization condition, after end of following dosing cycles. Then, the number and size of silver bromide crystals were established

increases the solubility of silver bromide (AgBr) and smaller crystals dissolve. Due to these processes, the overall number of crystals decreases, which results in lower turbidity value recorded, which can be clearly seen on the graphs (Fig. 4 and 5).

Reintroduction of silver nitrate (AgNO₃) solution portion, into the crystallising mixture, results in appearance of a new, thermodynamically unstable phase, able to recrystallise and deposit silver bromide onto larger, thermodynamically stable crystals. The overall number of crystals thus increases, resulting in increasing turbidity value. Due to the conditions of alternate reactant introduction being preferential for Ostwald recrystallisation, (Fig. 2), each dosing cycle stabilises the size and number of crystals. Both crystals size and count increase proportionately to time duration of synthesis, expressed as undertaking consecutive dosing cycles. Such a conclusion is confirmed by the predicted dependence of mixture turbidity and synthesis time, determined with good linear correlation, for $\lambda=600$ nm and plotted along with turbidity fluctuations on Fig. 5. The relation was determined at turbidity fluctuation minimum, after completing each full dosing cycle. These minima correspond to instantaneous, temporarily constant physicochemical conditions for Ostwald recrystallisation, in which crystals count and size varies in the dispersive mixture. In the course of the experiment, the 5 second long intervals separating consecutive dosing cycles were intentionally added, to document the successive stages of crystal size and count stabilisation, which take place after each dosing cycle.

Rayleigh scattering theory applies, by design, (e.g. [19-21]) to colloids containing spherical, non-absorbing particles, the size of which is smaller than the scattered wavelength at least by a factor of 10. By this

theorem, specific turbidity τ/c of a heterogeneous dispersive system, containing particles of size d, is proportional to the inverse of the fourth power of the scattered light wavelength λ, by equation: (1):

$$\frac{\tau}{c} = \frac{4}{\rho d}\left(\frac{\pi d \mu_0}{\lambda}\right)^4 \left(\frac{m^2-1}{m^2+2}\right)^2 \tag{1}$$

where:
c – particle concentration, [g/cm³],
λ – wavelength, [cm],
d – particle size, [cm],
m – relative refractive index, expressing the relation of refractive index of the dispersed phase to the refractive index of the continuous phase,
μ_0 – refractive index of continuous phase,
ρ – density of dispersed phase, [g/cm³].

Using the relation of instantaneous turbidity (Fig. 5) and suspension synthesis time, specific turbidity was calculated after each reactant dosing cycle. Using the obtained data and modified Rayleigh equation (1), in which constants determined at 20°C for wavelength $\lambda=600$ nm were used, the size of spherical particles forming in consecutive cycles was calculated (by equation 2):

$$d = \sqrt[3]{\frac{\tau}{c} \cdot \frac{\rho \cdot 2{,}303}{4 \cdot 10^4 \cdot 187{,}770} \cdot \left(\frac{\lambda}{\mu_0 \pi}\right)^4 \cdot \left(\frac{m^2+2}{m^2-1}\right)^2} = \tag{2}$$

$$17{,}9 \cdot \sqrt[3]{\frac{D_{600}}{C}} = 17{,}9 \cdot \sqrt[3]{T}$$

where:
d – particle diameter, [nm],
$\tau/c = 1000 \cdot 2.303 \cdot D_\lambda /l / M_{AgBr}$
l – dispersive layer thickness, [cm],
M_{AgBr} – molar mass of silver bromide, 187.770 [g],
$T = D_{600}/C$ – gradient of concentration function, determined at $\lambda=600$ nm, in a coordinate system described by optical density D_{600} and molar concentration C, [dm³/mol],
C – molar concentration of silver bromide, [mol/dm³],
D_{600} – optical density determined for $\lambda=600$ nm.

Determined spherical particles' diameter d was used to calculate length of the edge of a cube d_6, of the same volume [20] (3):

$$d_6 = \left(\frac{\pi}{6}\right)^{1/3} d \tag{3}$$

In the course of calculations, particle size changes have been determined (edge of cube, d_6) as a function of synthesis time (linear dependence in a semi-logarithmic coordinate system, Fig. 6). The relation thus determined shows good linear correlation in range of dosing cycles 4-15 (R=0.99714) and can be expressed by a linear equation (4):

$$d_6 = -33{,}8 + 33{,}2 \cdot Log(t), \pm 4\,nm \tag{4}$$

To ensure that the calculated values of crystals size were correct a series of tests were run based on the second mentioned method, using concentration method. Samples taken at cycles 5, 10 and 15 were diluted with distilled water and their spectral turbidity dependences were recorded. An example of the obtained turbidity on wavelength dependence function is shown at Figure 7, for the last dosing cycle, in which the final concentration of silver bromide (AgBr) was 0.375 mol/dm³.
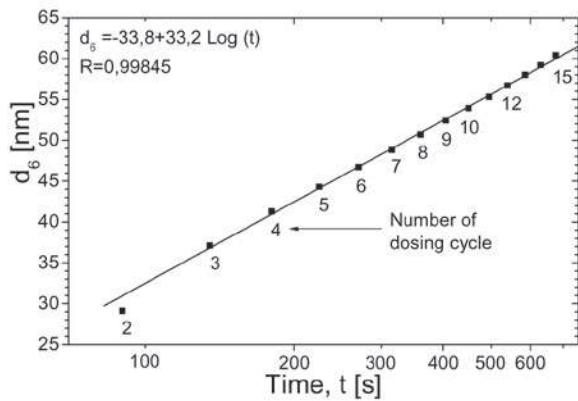
Fig. 6. Fluctuations in size of silver bromide cubic crystals during synthesis of silver bromide crystals suspension, from solutions of reactants of 1.0 mol/dm³ concentration

Fig. 8. Concentration curves of silver bromide crystals suspension calculated at the wavelength: 500, 600, 700 and 800 nm
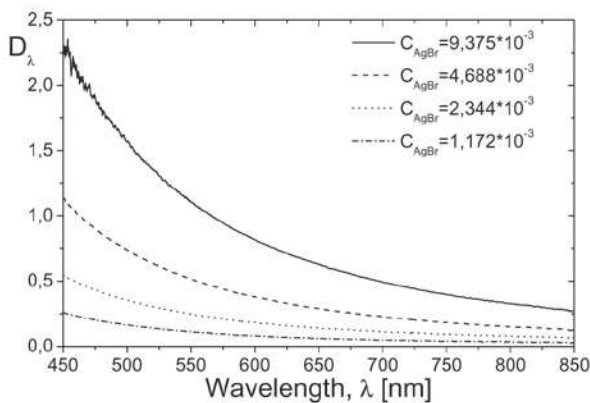

Fig. 7. Spectral dependence of optical density of silver bromide suspension measured for successive dissolutions of suspension prepared at the concentration reactants 1 mol/dm³. The process of synthesis suspension was carried out throughout 15 cycles

Fig. 9. The Rayleigh's equation expressed by relation between specific turbidity and $1/\lambda^4$

Based on spectral dependences obtained, concentration functions were plotted for a number of wavelengths in range of 500 to 800 nm (Fig. 8), and tangent (tan) was calculated for the angles of inclination. By *Rayleigh's* theorem, the values determined are proportional to specific turbidity τ/c, so they should also fulfil equation (1), in regard to the inverse of the fourth power of the wavelength. Figure 9 illustrates *Rayleigh's* relation calculated for the mentioned example, which demonstrates high affinity in wavelength range of 500 to 800 nm. It can be therefore assumed, that the heterogeneous systems, this work is concerned with, fulfil *Rayleigh's* scattering theorem, and furthermore, the results obtained from calculations based on this method are sufficiently accurate.

Using silver bromide (AgBr) crystals size measurements obtained after cycles 5, 10 and 15, a linear relation, possessing a high determination coefficient (R=0.99919) was calculated (equation 5) (Figure 10).

$$d_6 = -35,1 + 33,7 \cdot Log(t), \quad \pm 3,5 \; nm \qquad (5)$$

Fig. 10. Fluctuations in size of silver bromide cubic crystals during synthesis of silver bromide crystals suspension, from solutions of reactants of 1.0 mol/dm³ concentration. Size of growing crystals was measured after 5, 10, and 15 proportioning cycle.

Sufficient correlation between linear parameters of equations (4) and (5), obtained for a case of suspension synthesis using reactants solutions of 1.0 mol/dm³ concentration, as well as similarities between corresponding equations created for the other 7 experiments, points to a highly stable and fairly repeatable character of the investigated crystallisation processes. Taking into account the above conclusions and using the described scheme, a relation was evaluated between the size of silver bromide crystals (AgBr) in the final stage of the synthesis, as a function of the speed of reactant introduction, which in
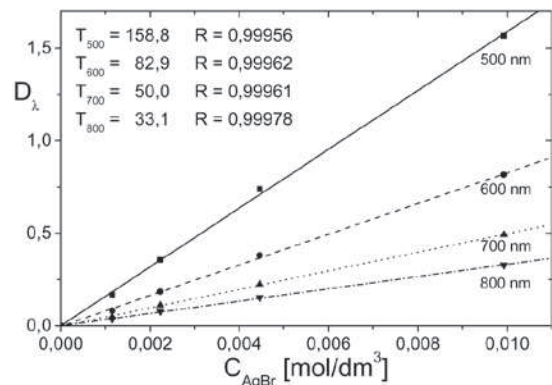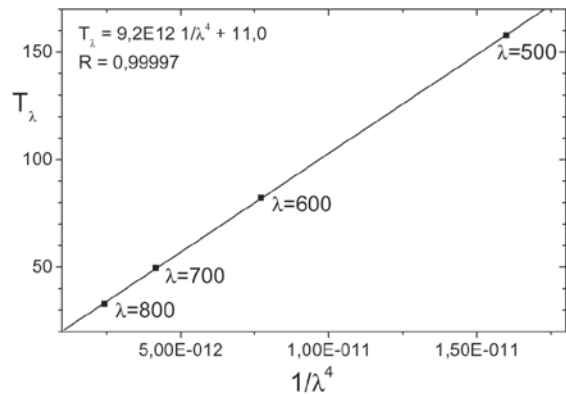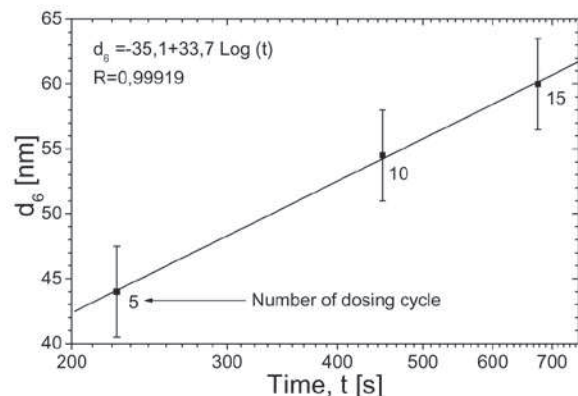

Fig. 10. Fluctuations in size of silver bromide cubic crystals during synthesis of silver bromide crystals suspension, from solutions of reactants of 1.0 mol/dm³ concentration. Size of growing crystals was measured after 5, 10, and 15 proportioning cycle

turn remains proportional to reactants concentrations, when using a stabilised dosing system. The relation mentioned above was based on average data obtained in a number of experiments (3 to 5), run for a known concentration of reagents in range of 0.4 to 3.5 mol/dm³. Resulting function was plotted and can be seen in Figure 11, with each plotted point representing an average value, which were in turn used to evaluate equation (6) with a high correlation factor (R=0.95563) by using linear regression.:

$$d_6 = 36,0 + 26,2 \cdot C, \quad \pm 5 \; nm \qquad (6)$$

Description of measurements

This work describes the dependence of reagents dosing into the dispersive mixture on the size of silver bromide crystals obtained. Research was conducted using a set synthesis scheme, while the only variable parameter was reactants concentration. After conducting 8 experiments using arbitrarily chosen values of reactants concentration, an average value was calculated from a number of results describing the dependence of silver bromide (AgBr) crystals size, produced in
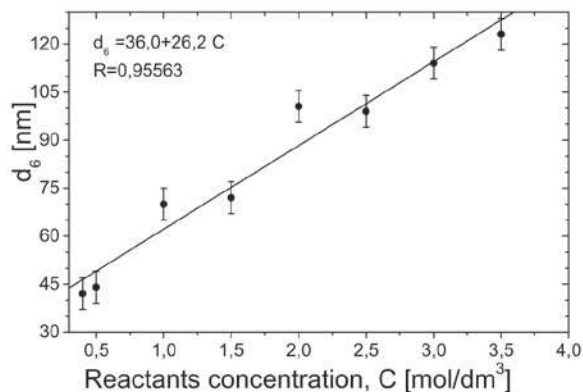
Fig. 11. Relation between the average size of silver bromide cubic crystals in the final stage of the synthesis, as a function of the speed of reactant introduction, which in turn remains proportional to reactants concentrations, when using a stabilised dosing system. Measurement was made in the end of synthesis process
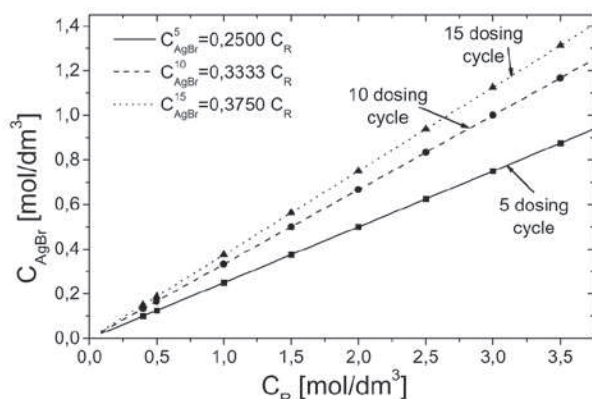

Fig. 12. Silver bromide concentration changes in suspensions after finishing dosing cycles 5, 10 and 15, evaluated as a function of concentration of reagents used in the synthesis. The suspension was prepared at the concentration reactants 1 mol/dm³

the final stage of the synthesis, on molar concentration of reactants. This relation was illustrated on Figure. 11 and written as equation (6), which demonstrates high linear correlation in the tested concentration range, and may serve as a basis for designing experiments using values from different ranges. Using the techniques used for measuring instantaneous crystals size during suspension synthesis, it was possible to ascertain the size of crystals at almost any given moment, except for the initial, thermodynamically unstable period, generally assigned to the first three reagents dosing cycles.

The relation presented shows that the use of reactants solutions of concentrations larger than 2.5 mol/dm³ results in such a rapid silver bromide crystals growth, that after finishing all 15 dosing cycles, crystals sizes exceed 100 nm. Therefore, to produce silver bromide suspensions suitable as substrates to synthesise sols of nanostructural silver, it is preferential to use reagents of concentrations no larger than 2.5 mol/dm³. Obtaining more subtle silver bromide crystals suspensions, of smaller final crystals size, i.e. smaller than 50 nm, requires reagent solution of concentrations not exceeding 0.5 mol/dm³. One substantial drawback of using diluted reagents solutions is the fact, that at the end of the process only a small concentration of silver bromide in the suspension is obtained. This, in turn, hinders obtaining highly concentrated silver sols, more interesting from the technical standpoint.

The final concentration of silver bromide present in the suspensions prepared using the assumed scheme, can be calculated using the approximated equation (7), which is a function of two technical parameters of the synthetic process: molar concentration of reagents, C_R and the number of finished dosing cycles, N, larger than 1:

$$C_{AgBr} = (0,0615 + 0,2700 \cdot Log(N)) \cdot C_R \qquad (7)$$

Figure 12 shows an example of silver bromide concentration

changes in suspensions after finishing dosing cycles 5, 10 and 15, evaluated as a function of concentration of reagents used in the synthesis. Simple calculations using equation (7) lead us to believe, that the same final concentrations of silver bromide in suspensions may be obtained by using reactant solutions of different concentrations and interrupting the synthesis in a given dosing cycle. It has to be considered, however, that both such cases are crystallisation processes in different physicochemical conditions, which results directly in different particle size distributions of created suspensions.

Analysing the precipitation process of sparingly soluble silver bromide from solutions of soluble salts, other factors, so far not included, that influence particle size distributions of forming crystals, come to mind. Those most important include: speed of mass exchange in volume of the reaction mixture, presence of factors increasing silver bromide solubility, ionic strength of reaction mixture, solutions viscosity, surface tension, presence of protective colloids, etc. However, the main factor influencing the speed of solid phase creation remains the solubility of the sparingly soluble salt and it's supersaturation in the reaction mixture. It is known that the speed of crystal seeds formation is a function of energy, connected with the creation of a new surface and is an exceptionally steep function of solution supersaturation. It can be thus assumed, that the speed of seeds formation is large under conditions of high supersaturation, and then rapidly decreases due to decreasing supersaturation, resulting directly from solid phase formation [22].

In conditions, in which ultra fine-crystalline suspensions are formed, the process is further made more complicated, due to the fact, that silver bromide is formed by a double displacement reaction between potassium bromide (KBr) and silver nitrate (AgNO₃). During mixing of highly concentrated reagent solutions, large differences between substrates concentrations exist, creating varied values of supersaturation in the reaction environment. The mechanism of the formation of thermodynamically stable crystal seeds is also further made more complicated, due to mass deposition on existing crystal seeds being a nonisotropic process.

At the moment of reaching theoretical equilibrium, in which crystal seeds size is equal to or larger than critical size, a certain number of thermodynamically stable seeds is formed - such seeds continue to grow as crystals. *Wagner's* equation demonstrates the number of crystal seeds normalised according to volume [22-24]:

$$Z = K \frac{SRT}{\sigma D V_m C_\infty} \qquad (8)$$

where:
K – constant of various values, depending on crystal seeding model assumed: $K=1.0/8\pi$ for Klein and Moisar's model [25], $K=3.0/8\pi$ for a model described by Kharitanova and others [26] and $K=1.0/5.9\pi$ for a model proposed by Sugimoto [27],
S – speed of reactants introduction, [mol·m⁻³·s⁻¹],
R – gas constant, [J·K⁻¹·mol⁻¹],
T – absolute temperature, [K],
σ – surface tension on the phases boundary, [J·m⁻²],
D – diffusion coefficient, [m²·s⁻¹],
V_m – molar volume, [dm³·mol⁻¹],
C_∞ – silver bromide solubility, [mol·dm⁻³].

By analysing this equation, we can see that the number of thermodynamically stable seeds is directly proportional to the speed of reactant introduction (concentration of substrates solutions) and inversely proportional to interphasal surface tension, diffusion coefficient of substrates, solubility of the solid phase and molar volume. It may seem, due to temperature term being present in the numerator of Wagner's equation that its increase should result in the increase of the number of stable crystal seeds. In practice, however, the inverse dependence is observed due to drastic changes of parameters' values present in the

numerator of this equation, mainly the diffusion coefficient, interphasal surface tension and solid phase solubility. Consequently, the lowering of the temperature of the seeding process is beneficial to the increasing number of stable crystal seeds with the simultaneous lowering of their size. These findings were used in practice of the experiments undertaken, conducting research at the temperature of 35ºC.

Conclusions

Analysing the results stemming from Wagner's equation and including relations illustrated on Figures 11 and 12 in further discourse, let us formulate conclusions, which lead us to state, that obtaining ultra fine crystal suspensions of silver bromide of possibly the smallest crystals size requires the use of sufficiently diluted reagents solutions. In such conditions silver bromide solubility in the crystallisation medium is appropriately small, which favours the formation of relatively small, stable crystal seeds, which in latter stages of synthesis grow to a size set by the number of dosing cycles. In turn, using concentrated reactant solutions results, even during a few first dosing cycles, in an increase in silver bromide solubility in the crystallisation medium, sufficient enough, that, according to Wagner's equation, the number of stable crystal seeds decreases, which in turn results in the significant increase of seed size. In consecutive stages of synthesis they increase to a size set by the number of dosing cycles, where the growth speed is smaller in the case of the larger crystal seeds than in the case of smaller ones.

The tests of long term stability of silver bromide suspensions stored in gel form at temperature lowered to 2ºC yielded important conclusions, the practical application of which allows for storing the obtained suspensions as gelatine based gels, without significant increases in crystals sizes.. The storage of gels containing post-synthetic potassium nitrate, the molar concentration of which is equal to the concentration of silver bromide, the more favours Ostwald recrystallisation, the larger the concentration is. The direct reason for undergoing recrystallisation in the stored gel is the so-called salt effect, in which increased solubility of silver bromide results from the presence of potassium nitrate. In this case silver bromide crystals growth is rapid enough, even at decreased temperature, that such storage methods are not recommended, it is further advised to remove unnecessary salts as quickly as possible, preferably soon after the synthesis. In case of the gels rinsed and stabilised by bromide ions to the minimum silver bromide solubility value, after 7, 14 and 21 days in storage no significant, larger than a few percent crystals size increase has been recorded, independently of concentration. To protect the gelatine from harmful bacteria, during storage in the freezer, it was preserved by addition of phenol at 0.01 g per 1 dm³ of suspension.

Using ultra fine-crystalline suspensions of silver bromide as a substrate for obtaining sols or nanosols of silver may only find use, when crystals of AgBr to be obtained do not exceed 100 nm in size, meaning reactant concentration of less than 2.5 mol/dm³. Obtaining more subtle silver bromide crystals suspensions, of smaller final crystals size, i.e. smaller than 50 nm, requires reagent solution of concentrations not exceeding 0.5 mol/dm³. However, one drawback of using such a method is the obtaining of suspensions of low final silver bromide concentration, which, in turn, makes the production of concentrated sols of silver, more interesting from the technical standpoint, difficult.

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Dr. Eng. *Agnieszka DYONIZY* graduated in 2001 from the Wroclaw University Faculty of Fundamental Problems of Technology (2001), Poland. Currently, she works in the Institute of Physical and Theoretical Chemistry at the University of Wroclaw. Specialization: Materials engineering.

Ph.D. Eng. *Piotr NOWAK* graduated in 1981 from the Wroclaw University Faculty of Chemistry, Poland. He obtained a Ph.D. degree in 2004. At the moment, he is a manager of the Division of Phototechnik in the Institute of Physical and Theoretical Chemistry at the University of Wroclaw. Specialization: Materials engineering.

Ms. Eng. *Agnieszka KRÓL-GRACZ* graduated in 2007 from the Wroclaw University Faculty of Chemistry, Poland. Currently, she is a PH.D. student at the Faculty of Chemistry in the Institute of Physical and Theoretical Chemistry at the University of Wroclaw. Specialization: Materials engineering.

Ms. Eng. *Ewa MICHALAK* graduated in 2008 from the Wroclaw University Faculty of Fundamental Problems of Technology, Poland, she is a PH.D. student at the Faculty of Chemistry in the Institute of Physical and Theoretical Chemistry at the University of Wroclaw. Specialization: Materials engineering.